

AD-755 259

A STUDY OF THE EFFECT OF CORONA
CONDITIONS ON ELECTROSTATIC PRINTING
PROCESSES

C. W. Frank, et al

Iowa University

Prepared for:

Army Engineer Topographic Laboratories

December 1972

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

AD 755259

ETL-CR-72-17

AD-

A STUDY OF THE EFFECT OF CORONA CONDITIONS
ON ELECTROSTATIC PRINTING PROCESSES
FINAL TECHNICAL REPORT

by

C. W. Frank
R. Buchacek

December 1972

Prepared for

U. S. ARMY ENGINEER TOPOGRAPHIC LABORATORIES

FORT BELVOIR, VIRGINIA 22060

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. Department of Commerce
Springfield, VA 22151

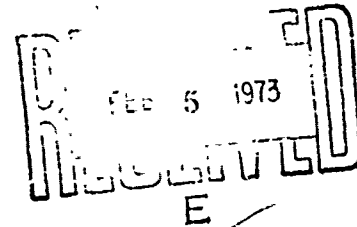
Prepared by

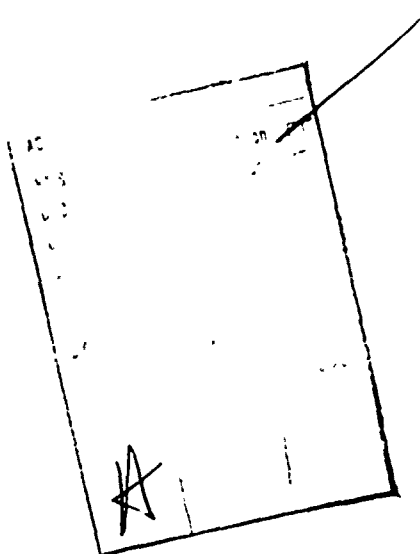
Department of Chemistry, University of Iowa

Iowa City, Iowa 52240

Contract No. DAAK02-72-C-0060

Approved for public release: distribution unlimited





NOTICES

Destroy this report when no longer needed
Do not return it to the originator.

The findings in this report are not to be
construed as an official Department of the
Army position unless so designated by other
authorized documents.

The citation in this report of trade names
of commercially available products does not
constitute official endorsement or approval
of the use of such products.

Unclassified
Security Classification

DOCUMENT CONTROL DATA - R & D		
(Security Classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author) University of Iowa, Department of Chemistry Iowa City, Iowa 52240		2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP
3. REPORT TITLE A study of the effect of corona conditions on electrostatic processes		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final technical report		
5. AUTHOR(S) (First name, middle initial, last name) C.W. Frank R. Buchacek		
6. REPORT DATE December 1972	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
8a. CONTRACT OR GRANT NO. DAAK02-72-C-0060	8b. ORIGINATOR'S REPORT NUMBER(S)	
9. PROJECT NO. 4A662707A852	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) ETL-CR-72-17	
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY U.S. Army Engineer Topographic Labs. Fort Belvoir, Va. 22060	
13. ABSTRACT <p>A study of those factors which can affect the quality of an electrostatic reproduction was undertaken. Observations were made under conditions which simulated the corona unit in Army electrostatic printers. The major areas of the study were: (1) corona configuration and charging homogeneity and, (2) environmental effect on the corona. The studies and conclusions have application to printing processes which employ corona discharge devices.</p> <p>The major recommendations which resulted from this research are: (1) develop a process in which a positive wire charging configuration can be used and, (2) develop a process which reduces the production of ozone in the unit.</p> <p>Details of illustrations in this document may be better studied on microfiche</p>		

DD FORM 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

Unclassified
Security Classification

1a

AD-

A STUDY OF THE EFFECT OF CORONA CONDITIONS
ON ELECTROSTATIC PRINTING PROCESSES

FINAL TECHNICAL REPORT

by

C. W. Frank
R. Buchacek

December 1972

Prepared for

U.S. ARMY ENGINEER TOPOGRAPHIC LABORATORIES

FORT BELVOIR, VIRGINIA 22060

Prepared by

Department of Chemistry, University of Iowa
Iowa City, Iowa 52240

Contract No. DAAK02-72-C-0060

Task No. 4A662706A85203

Approved for public release: distribution unlimited

IC

SUMMARY

A study of those factors which can affect the quality of an electrostatic reproduction was undertaken. Observations were made under conditions which simulated the corona unit in the Army electrostatic printers. The major areas of study were: (1) corona configuration and charging homogeneity and (2) environmental effect on the corona. The studies and conclusions have application to printing processes which employ corona discharge devices.

The major recommendations which resulted from this research are: (1) develop a process in which a positive wire charging configuration can be used and (2) develop a process which reduces the production of ozone in the unit.

FOREWORD

This work, done under Contract No. DAAK02-72-C-0060, was authorized by the U.S. Army Engineer Topographic Laboratories, Fort Belvoir, Virginia under DA Project-Task Area Work Unit No. 4A662707A85203/0013 Entitled "Corona Chemistry Studies for Military Map Reproduction".

A study was undertaken to determine those factors which influence the quality of the printing processes that use a corona discharge device.

The assistance of Mr. S. Shiffman, Ms. S. Tomkins, Ms. A. Becker, and Mr. R. Wall is acknowledged.

Mr. J. Gladden (USAETL) served as the Contracting Officer's Technical Representative.

TABLE OF CONTENTS

SUMMARY.....	ii
FOREWORD.....	iii
ILLUSTRATIONS.....	vi
TABLES.....	vii
I. <u>Introduction</u>	1
II. Investigation.....	1
A. <u>Corona Discharge Units</u>	1
A.1. Corona Unit Power Supplies.....	4
A.2. Ozone Sampling Technique.....	4
A.3. Isopar G Sampling.....	9
A.4. Roller Model Printer Prototype.....	9
A.5. Emission Spectroscopy.....	9
A.6. Electrostatic Charging Characteristics.....	13
A.7. Ion Current Measurements.....	13
III. <u>Results and Discussion</u>	15
A. Corona Unit Configuration and Electrode Polarity.....	15
A.1. Production of Ozone as a Function of Current-Voltage.....	15
A.2. Effect of Relative Humidity.....	17
A.3. Ozone Production as a Function of a Positive and Negative Corona.....	22
A.4. Effect of Isopar G on Ozone Production.....	26
B. Electrostatic Charging Characteristics.....	26

B.1. The Corona Discharge.....	32
B.2. Toner Pickup.....	33
B.3. Ion Currents.....	41
IV. <u>Conclusions</u>	46
A. Type of Charging Unit.....	46
A.1. Wire Charging Configuration.....	46
A.2. The Counter Electrode.....	46
A.3. A Positive Charging Configuration.....	46
A.4. Distance of Paper from Corona.....	50
B. <u>Environmental Effects</u>	50
B.1. Production of Ozone.....	50
C. <u>Major Recommendations</u>	51
C.1. Charging Configuration.....	51
C.2. Ozone Production.....	51
Literature Cited.....	52

ILLUSTRATIONS

1. General Representation of Corona Discharge Units.....	2
2. Charger Power Supply Circuit.....	5
3. Schematic Diagram of Sampling Apparatus.....	8
4. Model Corona Device.....	10
5. Emission Spectrum of Negative Corona.....	12
6. Schematic Diagram for Ion Current Determination.....	14
7. Ozone Production for Different Corona Configurations.....	21
8. Ozone Production in the Presence of Isopar G.....	28
9. Corona Emission Characteristics.....	34
10. Charging Characteristics I.....	35
11. Charging Characteristics II.....	36
12. Toner Pickup I.....	38
13. Toner Pickup II.....	40
14. Toner Pickup III.....	43
15. Toner Pickup IV.....	45
16. Typical Current-Voltage Characteristic of Corona.....	47
17. Current Density Profile of Corona.....	48
18. Time Dependence of Corona Discharge.....	49

TABLES

1. Dimensions of Corona Units.....	3
2. Production of Ozone as a Function of Corona Unit Configuration and Polarity.....	16
3. Production of Ozone as a Function of Current-Voltage.....	18
4. Ozone Production as a Function of Relative Humidity.....	23
5. Determination of Electrode Producing Ozone in a Double Corona Discharge Unit.....	25
6. The Production of Ozone as a Function of a Positive and Negative Corona.....	27
7. Electrostatic Charging Characteristics of Mean 8313 Paper.....	29

I. INTRODUCTION

Rapid electrostatic printing methods make use of corona discharges for placing an electrostatic charge on a photoconductive layer. In the case of the Army Five Color Map Printer, high power levels are required to charge the zinc oxide layer in order to obtain quality prints. Because of the corona current required, detrimental effects to the image can be expected. This study will show what effects corona configuration has on the printing process. Data is also presented to indicate the effect that the corona itself has on its surrounding environment.

In the studies utilizing a wire to wire corona discharge unit all attempts were made to ensure that experimental laboratory conditions approached those of the actual printer. When other corona discharge units were evaluated (point to plane, wire to plane, etc.), environmental conditions were kept the same so that a comparison of all units could be made. Also, these studies and conclusions apply not only to the zinc oxide process but to all printing processes which employ corona discharge devices.

Pertinent points covered by this study are comparison of the different types of corona discharge units (wire to wire; point to plane, wire to plane) with respect to:

- (1) production of ozone as a function of current.
- (2) charging homogeneity.
- (3) environment upon corona characteristics.

This report is divided into a number of sections which describe the experimental approach, results, and recommendations resulting from the research.

II. INVESTIGATION

A. Corona Discharge Units. Eight different types of corona discharge units were constructed for use in determining the various characteristics related to the electrostatic printing process. Figure 1 shows the fundamental design upon which all of these units are based. The complete specifications for each of these units is tabulated in Table 1.

To simulate the environmental conditions found during operation of the Army Five Color Map Printer, smaller, laboratory size versions of the full scale machine were used. The experimental observations were made using models of the Army Printer designed and built in these

FIGURE 1 GENERAL REPRESENTATION OF CORONA
DISCHARGE UNITS

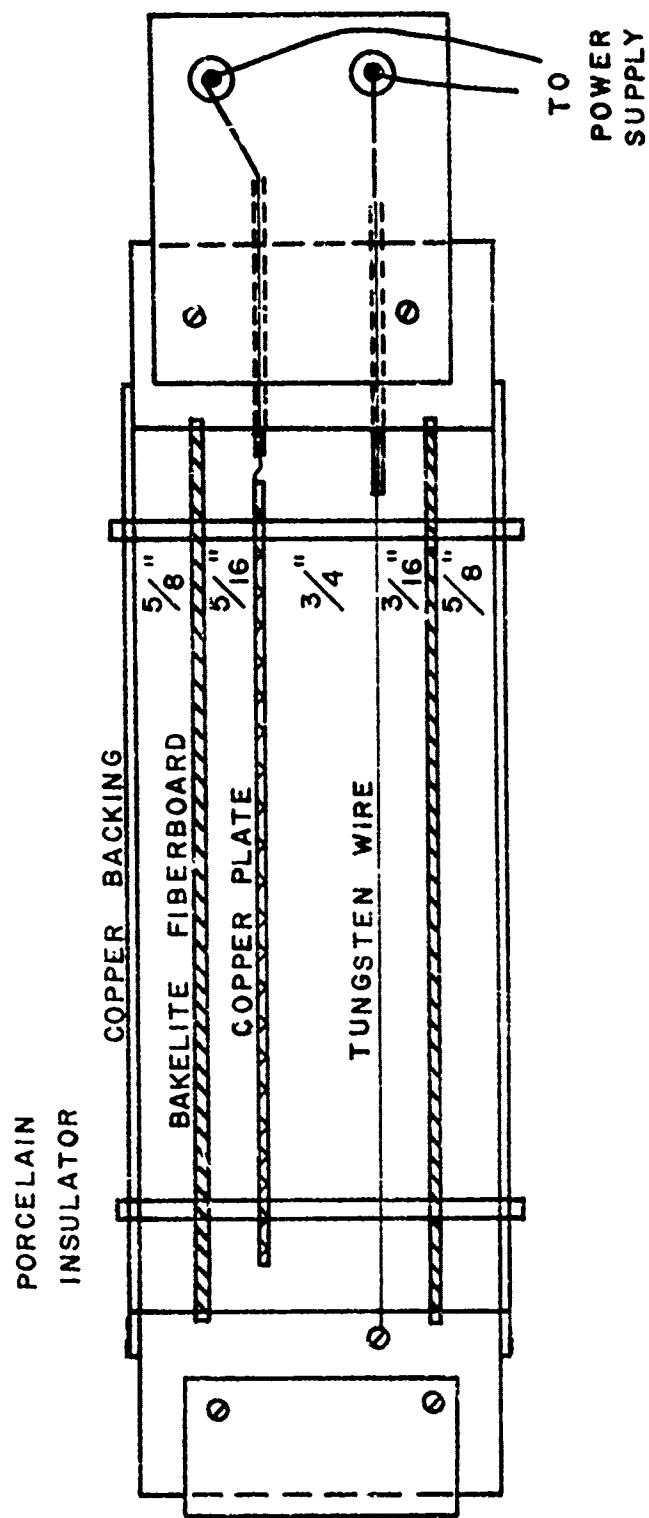


TABLE 1
Dimensions of Corona Units

Corona Unit	Electrodes ^a	Diameter of Wire Electrode, cm	Area of Electrode, cm ²
CDU #1	Tungsten Wire	0.013	0.80
	Tungsten Wire	0.013	0.80
CDU #2	Tungsten Wire	0.013	1.87
	Copper Plate	6.4x20.3	128.1
CDU #5	Tungsten Point ^b	0.013	0.006
	Copper Plate	6.7x23.0	152.1
CDU #6	Tungsten Wire	0.013	1.75
	Platinum Wire	0.025	3.50
CDU #7	Tungsten Wire	0.013	1.77
	Copper Wire	0.025	3.55
CDU #8	Tungsten Point ^c	0.013	0.060
	Copper Plate	10.0x20.0	200.0
CDU #9	Tungsten Wire ^d	0.013	1.87
	Copper Plate	6.5x20.0	130.0
CDU #10	Tungsten Wire ^e	0.013	0.80
	Tungsten Wire	0.013	0.80
CDU #11	Tungsten Wire ^e	0.013	0.80
	Copper Plate	6.0x20.0	120.0

- a) The distance between the electrodes is 1.90 cm.
- b) The electrode consisted of 48 tungsten wire points.
- c) The electrode consisted of 480 Tungsten wire points.
- d) The copper plate electrode is in the shape of a semi-cylinder.
- e) A plexiglass compartment was constructed about this electrode.

laboratories. Some of the other electronic and mechanical equipment were purchased from commercial suppliers. The unit was designed to compare the properties of the different corona discharge units. Such characteristics as ozone production and platin charging capabilities for all units were determined using this device.

A.1. Corona Unit Power Supplies. Two of the power supplies used in this work were constructed during the previous contract. Direct current (DC) power supplies suitable for operating the double corona discharge units were obtained from two sources. The power supply used in the earlier work was designed and constructed after studying information obtained from Wabash Magnetics, Inc., and following a description of the power supply used in the Michle-Goss-Dixter version of the Army Printers. Parts for the high voltage - constant current power supply were obtained from Wabash Magnetics and from parts on hand in these laboratories. A 9000 VAC "Luminous Tube Transformer" (General Electric) was used as the voltage step-up portion of the power supply. Output voltage was a maximum of 18 KVDC from this "voltage doubler" power supply at up to 1.0 milliampere of current. A continuously variable voltage transformer ("Variac") was used to energize the power supply.

Another power supply was purchased from Electromagnetic Products, (#T-51753C) Division of Wabash Magnetics, Inc., which has essentially the same characteristics as the noncommercial unit and was used in some of the later experiments.

In addition, two other power supplies were constructed. These are identical with those previously described with the exception that an Allanson rather than a General Electric luminous tube transformer was employed. The circuit diagram which produces the half-wave rectified output signal is shown in Figure 2.

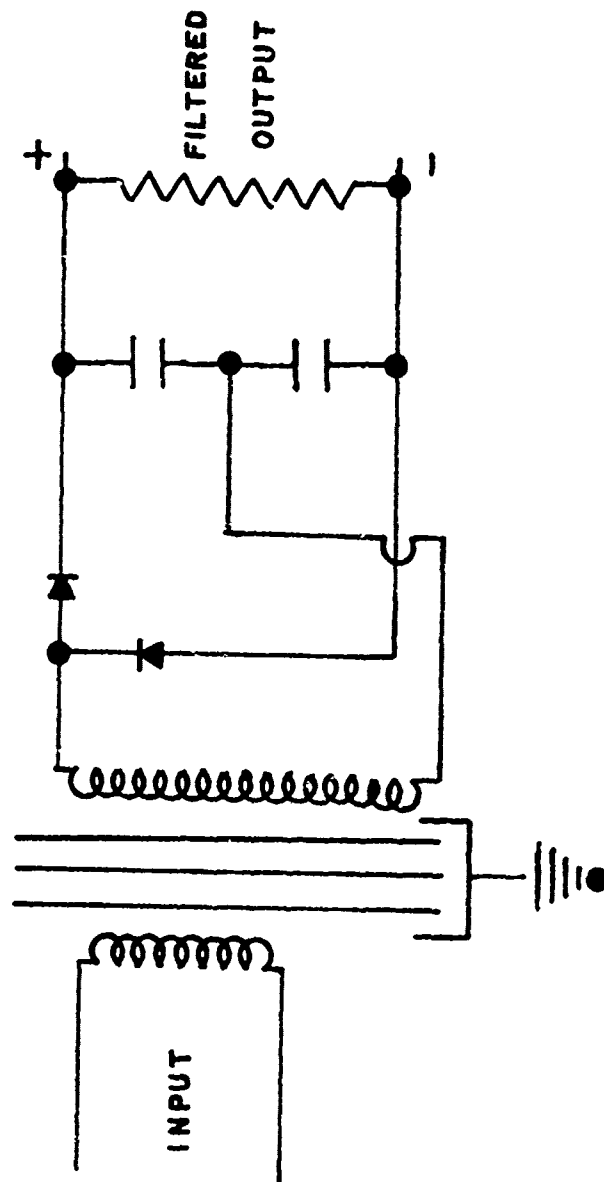
Hereafter corona discharge unit will be abbreviated CDU.

A.2. Ozone Sampling Technique. One of the detectable products which results from a corona discharge in the atmosphere is ozone. Thus, a knowledge of the factors which affect the production of ozone would be of interest in characterizing some of the processes which occur in electrostatic printing.

To measure the concentration of ozone produced, the corona discharge units were monitored within a chamber. The chamber was constructed using the basic "Chromatocal", (Model A125, Reco Division Research Specialities) which allows for the control of atmospheric conditions surrounding the CDU.

FIGURE 2

CHARGER POWER SUPPLY CIRCUIT



A schematic diagram of the apparatus employed for ozone analysis is shown in Figure 3. In a typical experiment, the desired atmospheric conditions were adjusted and the corona unit was then initiated. After a period of ten minutes, a sample of gas was withdrawn from the chamber, trapped, and analyzed iodometrically for ozone content. The size of the sample withdrawn for analysis represents approximately 2% of the total chamber volume. The concentration of ozone was calculated as ppm of air in the chamber by means of equation 1 (1).

$$\text{ppm } O_3 = \frac{(V) (24) (N_{Na_2S_2O_3})}{(V_o) (d) 1000} \quad 1$$

where,

V is the volume $Na_2S_2O_3$.

24 is the equivalent weight of ozone (g/eq).

N is the normality of $Na_2S_2O_3$.

V_o is the volume of gas sample withdrawn from the chamber (2 liters).

d is the density of air (1.268 g/l).

Ozone concentration values were determined by a standard potassium iodide - sodium thiosulfate titration procedure (2). Typically, two liters of corona chamber atmosphere (being stirred with a small fan to insure uniform sampling) were passed through a gas bubbler vessel containing 100 ml of 2% potassium iodide solution. The "Varistaltic" pump used to circulate chamber gases was capable of flow rates of up to 1.5 liters per minute (usually < one l/min) as measured by a gas flowmeter (Brooks Instruments Co.). A two liter gas ballast vessel was placed next to the suction part of the pump, and preceded by the gas bubbler vessel, flowmeter, and then the corona chamber, in that order (Figure 3). Iodide ion is oxidized by ozone to free iodine and this is then titrated with standard sodium thiosulfate solution using starch as the indicator (2). The ozone concentration values were calculated and recorded in parts per million of O_3 and plotted vs time.

Legend to Figure 3

Corona Chamber.....	Chromatocab Model A125 Reco Division, Research Specialties.
Hygrometer.....	Amlab Inc., Model H
Flowmeter.....	Brooks Instrument Company
Pump.....	Manostat varistaltic pump
Gas Chromatograph.....	Bendix 2100
Column.....	5% OV-1 on 60-80 mesh Chromosorb W
Recorder.....	Honeywell Electronic 194

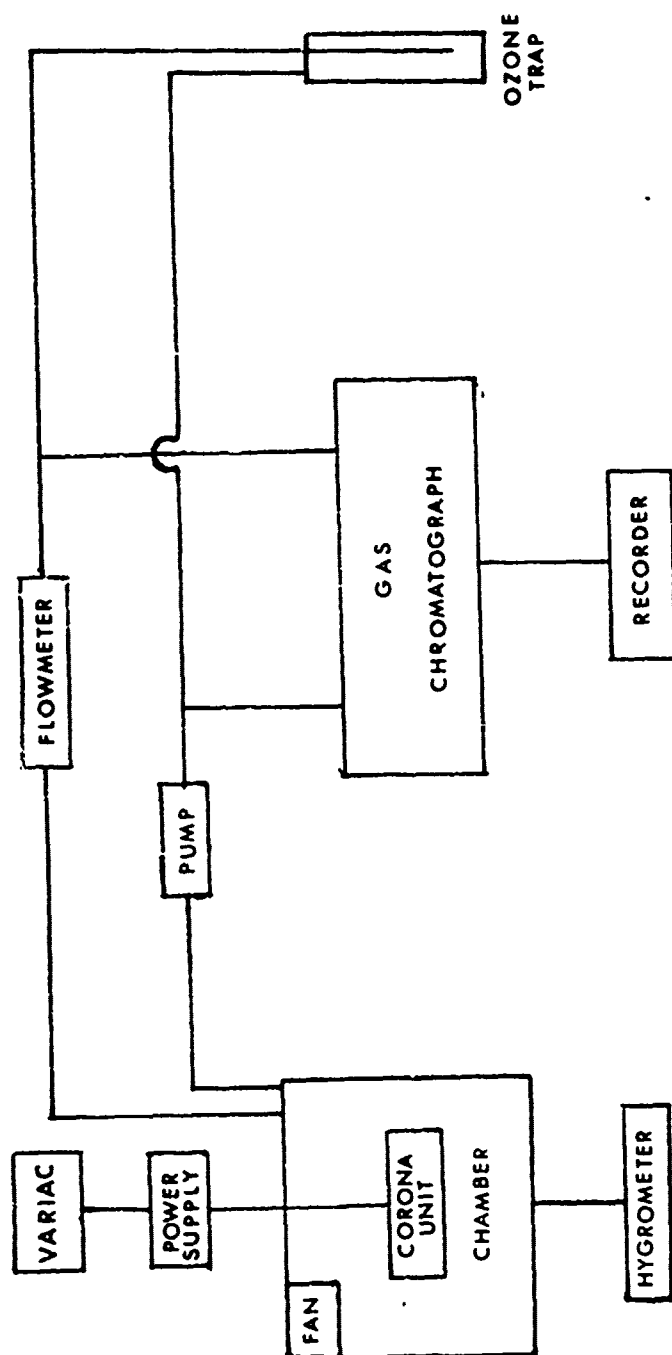
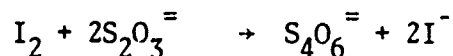


FIGURE 3 SCHEMATIC DIAGRAM OF SAMPLING APPARATUS



A.3. Isopar G Sampling. The Isopar G concentration in the corona chamber was determined by gas chromatography using a 5% OV-1 on 60-80 mesh Chromosorb W column. The atmosphere was sampled by a flow system in which the gas was pumped through a standard volume gas injection system connected to the gas chromatograph. Injection into the column was automatically controlled for sampling at prescribed time intervals. Calibration of the gas chromatographic detector was accomplished by syringe injection of measured amounts of Isopar G.

A.4. Roller Model Printer: Prototype. Corona discharge units were mounted in a four roller apparatus constructed with 1/4" thick Bakelite sidewalls. The roller axles were 1/2" aluminum rod stock and the rollers were 1 1/2" capped copper pipes. The drive roller was turned by a small electric motor through a reduction gearbox so that the continuous web moved at a linear speed of 4 1/2" per second.

A constant tension was applied to the paper web through the variable position idler roller which applied pressure by use of a spring loaded roller mount as shown in Figure 4.

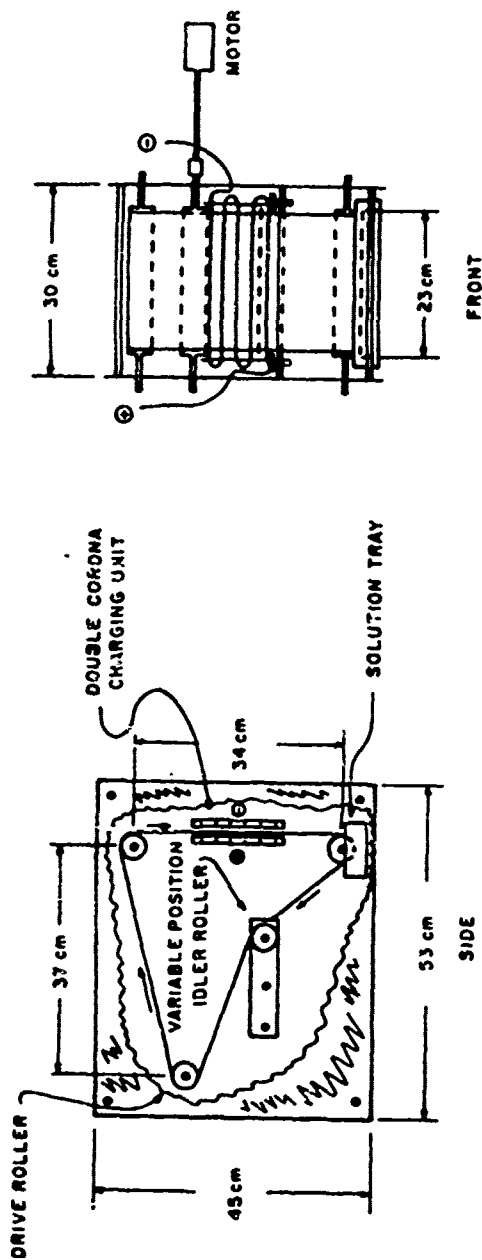
A.5. Emission Spectroscopy. Attempts have been made to identify the excited species produced in a corona discharge by means of their emission spectra. The instrument employed was a Sargent-Hilger Cornu Mount quartz spectrograph. This low resolution instrument has a dispersion of 8.3 Å/mm at 250 nm and 28.5 Å/mm at 400 nm (3). Kodak SA-1 and 103 aD photographic plates were employed to record the spectra of the excited species emission. The sensitivity range of the SA-1 is 200 nm to 400 nm, and that of the 103 aD is 200 nm to 625 nm.

The photographic plates were calibrated with the standard copper lines from a copper hollow cathode discharge tube. The corona discharge emission spectrum was recorded for exposure times as short as one hour and as long as seventy-two hours. A typical spectrum is presented in Figure 5.

Linear interpolation of the line spectra obtained was accomplished by using the Hartmann Dispersion Formula (4,5). For wavelength calculation, it is represented by the following equation:

A-671-300

FIGURE 4



A MODEL CORONA DEVICE - A SIMULATED ELECTROSTATIC
PRINTER

DESIGNED BY C.W. FRANK, E.E. GREEN, AND G.B. DREHER
OCT. 7, 1970

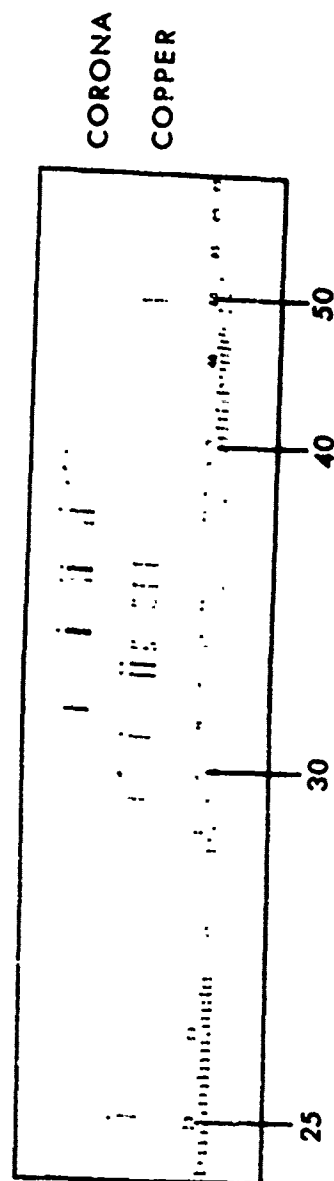
Legend for Figure 5.

Two spectra are presented in this figure.

Corona is the emission spectrum (N_2) of the negative glow of a wire corona.

Cu is a standard comparison of a copper arc.

FIGURE 5 EMISSION SPECTRUM OF
NEGATIVE CORONA



$$\lambda = \lambda_0 + \frac{C}{(d_0 - d)^{1.2}}$$

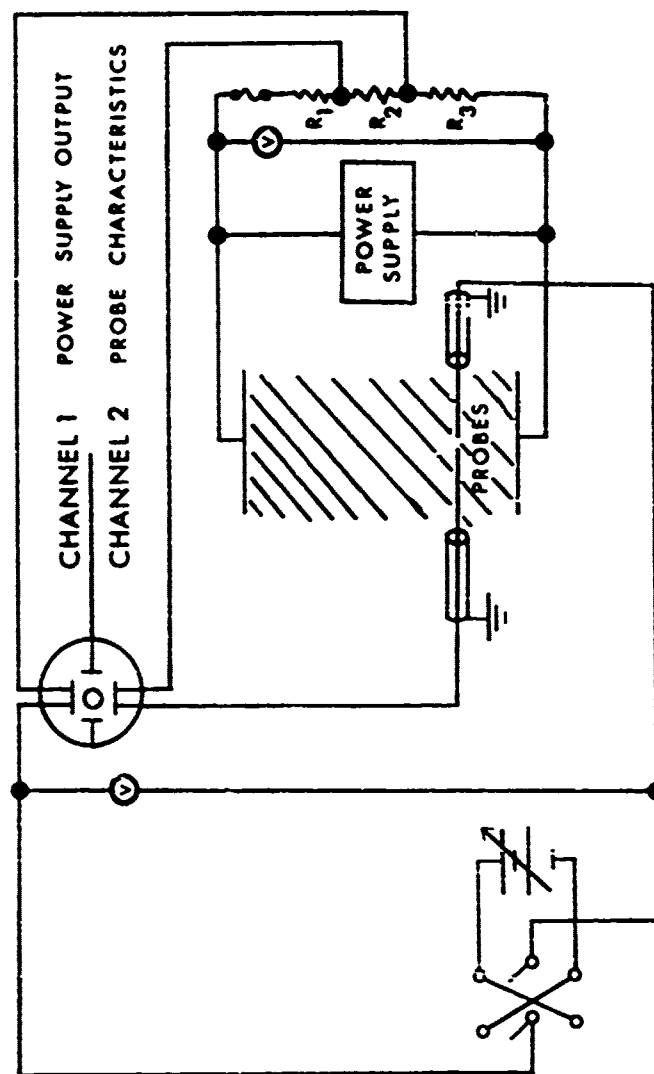
The constants λ_0 , C , and d_0 are determined from calibration of a standard spectrum. The wavelength, λ , after calibration, can be determined by measuring the distance, d , of the line from the reference point, d_0 .

A.6. Electrostatic Charging Characteristics. Two methods were employed to determine the charging characteristics of several corona discharge units. The first method involved directly measuring the static potential charge developed on Vean 8313 EP paper by means of a Keithley Model 610CR electrometer equipped with a remote static head detector. The detector had a 10,000:1 capacitive division which allowed potentials up to 20KV to be measured. The electrometer output was fed into a Moseley Model recorder and recorded directly.

The second method employed to determine the charging characteristic of the corona discharge units involved charging the Vean 8313 EP paper and developing the paper with a green toner suspension. The toner RU-99A, Interchemical Corporation, was diluted with Isopar G (Humble Oil and Refining Co.) in the ratio of 10,000:1 Isopar G: toner solution.

A.7. Ion Current Measurements. Measurements of ion currents (6,7,8,9) were made using the apparatus shown in Figure 6. The corona device was a point to plate apparatus operating at a voltage of approximately 9000 Volts. A constant D. C. voltage was applied across the probes with the D.C. power supply, Heathkit Model PS-4. This applied voltage was measured with the digital voltmeter, Beckman Model 4011. The current through the probes was measured on one channel of the storage oscilloscope, Tektronix model 549, as a voltage drop across the internal one megohm resistance. At an oscilloscope scan rate of 10 milliseconds per centimeter over the 10 cm. screen, a 100 millisecond scan was made. This equals approximately six cycles of the 60 cycle per second plasma power supply. Immediately after scanning the probe current and storing the scan on the oscilloscope, the applied voltage was reversed, the oscilloscope scan was offset approximately .5 cm. to eliminate overlap, and a second measurement was made. Measurements were made at applied probe voltages from -100 V to +100 V. The distance from the points (of the point to plate corona) to the probes was varied in one millimeter increments. No measurement could be made within 2 mm. of the points because arcing between the corona and the probes

FIGURE 6 SCHEMATIC DIAGRAM FOR
ION CURRENT DETERMINATION



resulted. At probe to point distances more than 8 mm probe response was not great enough to be significant. In addition, measurements were made directly beneath one of the points since it was found that any lateral displacement from this position reduced probe response to an unusable level. After two scans had been made they were photographed from the oscilloscope screen using a polaroid camera. The maximum deflection of each peak in the probe response scans was measured using a floating microscope. Corrections were made for the reduction in image size during photographing. The average measured deflection was then converted to current in microamps. The difference between the deflections caused by the positive and negative applied potentials was then divided by two to give the deflection caused by the applied voltage versus zero applied voltage. The resulting current versus applied voltage relationships were plotted.

III. RESULTS AND DISCUSSION

A. Corona Unit Configuration and Electrode Polarity. The production of ozone was evaluated in terms of the various corona unit configurations described in Table 1. These results are presented in Table 2. In each case, the ozone reported is in terms of the maximum equilibrium concentrations produced.

In those experiments at a current of 0.10 mA, in which CDU #1, CDU #6 and CDU #7 were employed, the production of ozone appears to be little affected by electrode polarity. In addition, the amount of ozone produced by these units are quite comparable. This is in contrast to results obtained from CDU #2 and CDU #5 in which the electrode polarity and corona configuration have a large effect on the resulting ozone produced.

Another point of interest for CDU #2 and CDU #5 is that when wire and points are of the same polarity significantly different concentrations of ozone are produced. This surprising observation is not at this time understood.

A.1. Production of ozone as a function of current-voltage. There are three generally accepted mechanisms for the formation of ozone. All of these include formation of molecular oxygen, excitation, dissociation and/or ionization. The equation which represents these possible mechanisms are shown below.

1. Excitation

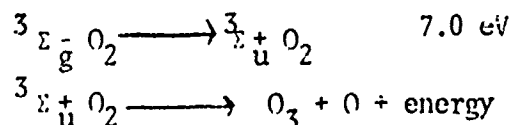
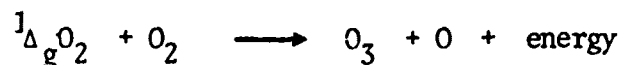
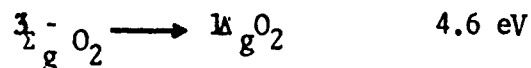


Table 2

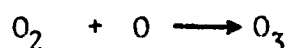
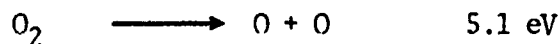
Production of Ozone as a Function of
Corona Unit Configuration and Polarity

Corona Unit	Electrode Polarity	%RH ^b	Max. ^c ppm O ₃	Electrode Surface Area, Cm ²
CDU #1	-	18%	25 \pm 3	Wire - 0.80
CDU #2	W-wire- Cu-plate +	18%	8 \pm 1	Wire = 1.87 Plate = 128.1
	W-wire + Cu-plate-		21 \pm 3	
CDU #5	W-points- Cu-plate+	18%	25 \pm 3	Points = 0.005 Plate = 152.1
	Pt-wire- W-wire +	18%	24 \pm 3	Pt = 3.50 W = 1.75
CDU #6	Pt-wire+ W-wire-		16 \pm 3	
	Cu-wire- W-wire+	18%	30 \pm 3	Cu - 3.55 W = 1.77
	Cu-wire+ W-wire-		27 \pm 3	
CDU #8	W-Points- Cu-Plate+	18%	10.0 \pm 2	Points = 0.060 Plate = 200.0
	W-Points+ Cu-Plate-		1.5 \pm .5	

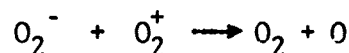
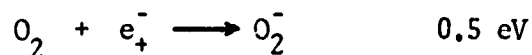
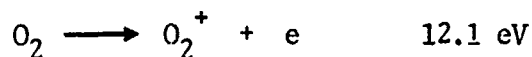
- a) The current was 0.1 mA in each experiment.
 b) The relative humidity was maintained to \pm 5%.
 c) The errors represent the average deviations for replicate experiments.



2. Dissociation



3. Ionization



In the first mechanism the energy is added to the oxygen molecule to form an excited species 7.0 eV above the ground state. The active oxygen ($^3\Delta_g^-$) subsequently reacts with a ground state oxygen molecule to form ozone and an oxygen atom. Similarly, the oxygen molecule can be excited to a state 4.6 eV above the ground state ($^1\Delta_g$) which can again form ozone and an oxygen atom.

The second mechanism involves addition of energy (5.1 eV) which results in the formation of two oxygen atoms which can react with an oxygen molecule to form ozone. The third scheme indicates the production of both positively charged and negatively charged oxygen species. These, subsequently, combine to form ozone and an oxygen atom.

In each case the reactions are initiated by an input of energy forming an active intermediate with the subsequent formation of ozone. Therefore, the higher the initial energy input, the more reactive intermediate and ozone produced. The results are listed in Table 3 and shown graphically in Figure 7.

A. 2. Effect of Relative Humidity. An increase in relative humidity results in two major observations. First, a drastic decrease in ozone concentration is observed with an increase in the relative humidity. Second, lower voltages are necessary to produce the same currents as those at lower relative humidities.

Table 3
Production of Ozone as a Function of
Current-Voltage

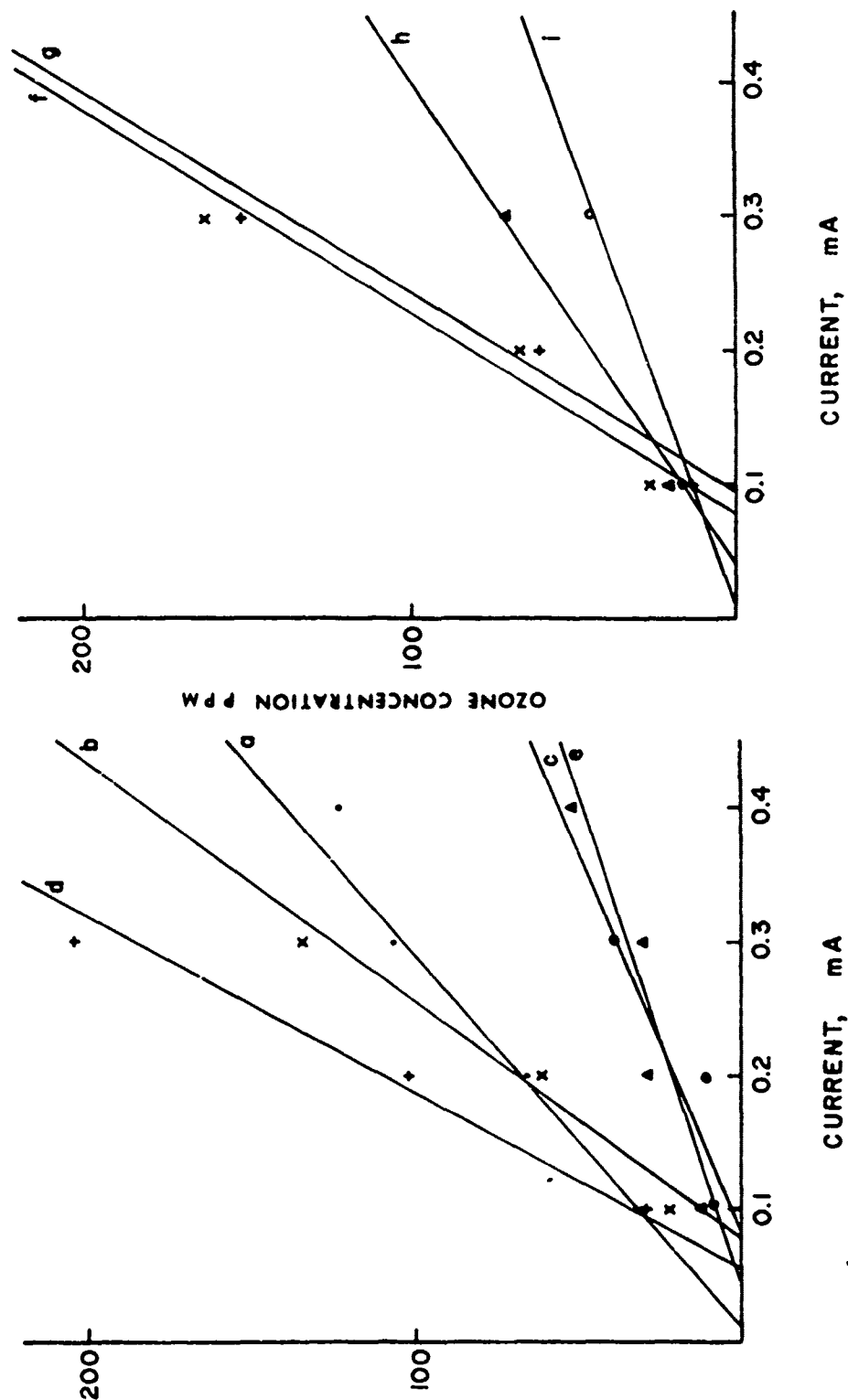
<u>Corona Unit</u>	<u>Electrode Polarity</u>	<u>Current mA</u>	<u>Applied Voltage</u>	<u>O₃ ppm</u>	<u>% RH</u>
1	-	0.1	12,000	31.8	25
1	-	0.2	13,500	87.4	25
1	-	0.3	14,000	107.0	25
1	-	0.4	15,000	132.8	25
2	Wire+				
	Plate-	0.1	13,500	21.7	17
	Wire-				
2	Plate+	0.1	13,500	7.4	16
	Wire+				
2	Plate-	0.2	14,700	61.0	18
	Wire-				
2	Plate+	0.2	14,700	7.3	18
	Wire+				
2	Plate-	0.3	15,700	134.6	18
	Wire-				
2	Plate+	0.3	16,400	39.1	18
	Points+				
5	Plate+	0.1	10,000	29.2	17
	Points+				
5	Plate-	0.1	10,000	11.1	17
	Points-				
	Plate+	0.2	11,200	101.9	18
	Points+				
5	Plate-	0.2	13,300	28.2	18
	Points-				
5	Plate+	0.3	12,000	204.7	18

5	Points+ Plate-	0.3	14,700	29.1	18
5	Points- Plate+	0.4	12,200	252.0	18
5	Points+ Plate-	0.4	16,500	52.8	18
6	Point- Wire_	0.1	10,300	23.6	17
6	Point+ Wire-	0.1	10,300	16.0	17
6	Point- Wire+	0.2	12,200	65.5	18
6	Point+ Wire-	0.2	12,500	60.0	18
6	Point- Wire+	0.3	13,200	161.9	18
6	Point+ Wire-	0.3	13,200	145.6	18
7	Cu- Wire+	0.1	11,000	30.3	18
7	Cu+ Wire-	0.1	11,000	27.8	18
7	Cu- Wire+	0.3	12,000	70.0	18
7	Cu+ Wire-	0.3	12,200	41.9	18

Legend to Figure 7

<u>Plot</u>	<u>CDU Number</u>	<u>Point Designation</u>	<u>Comments</u>
a	1	.	
b	2	x	wire + plane -
c	2	o	wire - plane +
d	5	+	points - plane +
e	5	Δ	points + plane -
f	6	x	Pt wire- W wire +
g	6	+	Pt wire + W wire -
h	7	Δ	Cu wire - W wire +
i	7	o	Cu wire + W wire -

FIGURE 7 OZONE PRODUCTION FOR DIFFERENT
CORONA CONFIGURATIONS



Two arguments which would be consistent with the observed decrease in ozone formation at higher relative humidities are the following: in one instance, the water vapor is acting as a scavenger for the ozone formed, secondly, the water vapor is directly scavenging the reactive ozone precursors. A further discussion of this point will be made later in this report.

It has been suggested (10) that at higher relative humidities formation of water clusters ($[\text{H}_2\text{O}]_n$) occurs. It has also been theorized that these clusters of water molecules have a lower ionization potential than a single water molecule. Therefore, our observation of an equivalent current at lower voltages under conditions of increasing relative humidity is consistent with this argument. The results are shown in Table 4.

A.3. Ozone Production as a Function of Positive and Negative Corona. This portion of the study deals with determining whether ozone is produced at the positive electrode or negative electrode in a corona discharge. Two types of experiments were carried out to determine this characteristic. First, a special corona unit was constructed to ascertain which electrode produced ozone in a double corona discharge. Second, the amount of ozone produced by positive and negative coronas was determined.

Corona units CDU #10 and CDU #11 were designed for the purpose of determining which electrode produces ozone in a double corona discharge. CDU #10 is essentially a tungsten wire to wire unit. A plexiglass compartment, containing a sampling port, was constructed about one of the wire electrodes. Since a corona discharge could not be sustained when the electrodes were completely separated from one another an opening was cut in the plexiglass which separated the wire electrodes. The size of the opening was regulated by placing a piece of paper, containing a 0.5 x 4.5 cm slit, over the opening. Corona unit CDU #11 is essentially the same as CDU #10, with the exception that the non-sampling wire electrode was replaced by a copper plate. To eliminate or at least reduce the diffusion of ozone into the sampling chamber a stream of air was passed over the non-sampling electrode. The results of these experiments are summarized in Table 5.

The results indicate that ozone is produced at both the positive and negative electrodes. The data also show that more ozone is produced at the positive electrode than at the negative electrode in a double corona discharge. The result is not surprising, since at liquid nitrogen temperatures, ozone was found only in the positive column of a glow discharge (11).

Table 4
Ozone Production As A Function of
Relative Humidity

<u>Corona Unit</u>	<u>Electrode Polarity</u>	<u>Current mA</u>	<u>Applied Voltage</u>	<u>O₃ ppm</u>	<u>% RH</u>
2	Wire- Plate+	0.1	13,500	7.4	18
2	Wire+ Plate-	0.1	13,500	21.7	17
2	Wire- Plate+	0.1	3,000	0.0	48
2	Wire + Plate -	01.	2,200	0.0	46
2	Wire- Plate +	0.1	1,800	0.0	64
2	Wire + Plate -	0.1	1,800	0.0	70
5	Points- Plate +	0.1	10,000	29.2	17
5	Points + Plate -	0.1	10,000	11.1	17
5	Points - Plate +	0.1	--	20.1	41
5	Points + Plate -	0.1	--	0.0	52
6	Pt - Wire +	0.1	10,300	23.6	17
6	Pt + Wire -	0.1	10,300	16.0	17
6	Pt + Wire -	0.1	6,200	0.0	48
6	Pt- Wire +	0.1	6,900	0.0	49
6	Pt + Wire -	0.1	2,200	0.0	86

6	Pt - Wire +	0.1	2,200	0.0	84
7	Cu- Wire +	0.1	11,000	30.3	18
7	Cu + Wire -	0.1	11,000	27.8	18
7	Cu + Wire -	0.1	7,200	0.0	66
7	Cu - Wire +	0.1	8,200	0.0	75
7	Cu + Wire -	0.1	4,500	0.0	85
7	Cu - Wire +	0.1	5,200	0.0	85

Table 5
Determination of Electrode Producing
Ozone in a Double Corona Discharge Unit

<u>Corona Unit</u>	<u>Total Applied Potential</u>	<u>Current mA</u>	<u>Sampling Chamber Polarity</u>	<u>ppm</u>
CDU #10	15,500	0.1	Positive	5.34 ^a
"	"	"	Negative	1.55 ^a
"	"	"	Negative	0.46 ^b
"	"	"	Positive	1.49 ^b
"	"	"	Positive	1.08 ^{b,c}
"	"	"	Negative	0.00 ^{b,c}
"	"	"	Negative	0.43 ^d
"	"	"	Positive	4.26
CDU #11	"	"	Negative	0.00 ^a
"	"	"	Positive	0.20 ^a
"	"	"	Positive	0.00 ^b
"	"	"	Negative	0.64 ^b

- a) No paper restriction between electrodes and no air flow passing over non-sampling electrode. Dimensions of the oval opening 2.5 x 4.5 cm.
- b) Paper restriction placed over oval opening. No air flowing over non-sampling electrode.
- c) Removed copper ground plate.
- d) No paper restriction between electrodes and air flow flushing non-sampling electrode.

The second set of experiments was designed to determine the ozone produced by a positive and a negative corona. A positive corona is defined as having a high positive potential applied to the active electrode and the other electrode at ground potential. A negative corona results from the application of a high negative potential to the active electrode and the other electrode at ground potential. The amount of ozone produced by these two configuration is shown in Table 6.

An examination of the results shown in Table 6 would suggest that the formation of ozone is independent of corona configuration. That is, comparable amounts of ozone are produced in both the positive and negative corona discharges.

A.4. Effect of Isopar G on Ozone Production. The results of this study are shown graphically in Figure 8. These results indicate that the formation of ozone is impeded by the presence of Isopar G. Furthermore, the maximum concentration of ozone produced in these experiments is inversely proportional to the initial concentration of Isopar G.

Since these experiments were done at constant relative humidity, this suggests that Isopar G is acting as a scavenger of an ozone precursor or is reacting directly with the ozone formed. It is also shown in Figure 8 that at a constant Isopar-G concentration and higher relative humidity, the amount of ozone produced is drastically reduced. This perhaps is not surprising since it already has been shown that the relative humidity affects ozone production

B. Electrostatic Charging Characteristics. The electrostatic buildup on the Mead 8313 paper was measured directly as a function of corona unit configuration and relative humidity. The three different corona units selected were CDU #1 (wire to wire), CDU #2 (wire to plate) and CDU #5 (point to plate). The results are shown in Table 7.

These results illustrate a number of interesting phenomena of the three discharge devices. 1) The static potential of the Mead paper may be positive or negative, depending on whether the ZnO layer is facing the positive or negative electrode. 2) an increase in relative humidity drastically reduces the charge on the paper. 3) The amount of static charge is a function of applied potential. 4) The time required to reach maximum charge is instantaneous. 5) If the oxygen content of the chamber is increased, the paper appears to charge to a greater extent. 6) It was also noted that when the corona was turned off the charge on the paper was almost completely dissipated within five minutes. 7) The positive and negative

Table 6
The Production of Ozone as a Function
of a Positive and Negative Corona

<u>Total Applied Potential Volts</u>	<u>Current mA</u>	<u>%R H</u>	<u>Electrode Polarity</u>	<u>ppm O₃</u>
12,000 ^a	0.10	25	Electrode 1-Negative Electrode 2-Positive	31.8
-6,700	0.10	25	Electrode 1-Ground Electrode 2-Negative	4.1
-7,700	0.15	26	Electrode 1-Ground Electrode 1-Negative	9.1
-8,400	0.20	25	Electrode 1-Ground Electrode 1-Negative	20.5
-8,400	0.30	80	Electrode 1-Ground Electrode 2-Negative	15.0
+6,700	0.10	26	Electrode 1-Ground Electrode 2-Positive	6.8
+7,700	0.15	25	Electrode 1-Ground Electrode 2-Positive	15.9
+8,400	0.20	25	Electrode 1-Ground Electrode 2-Positive	27.3

a) Double Corona.

FIGURE 8 OZONE PRODUCTION IN THE
PRESENCE OF ISOPAR G

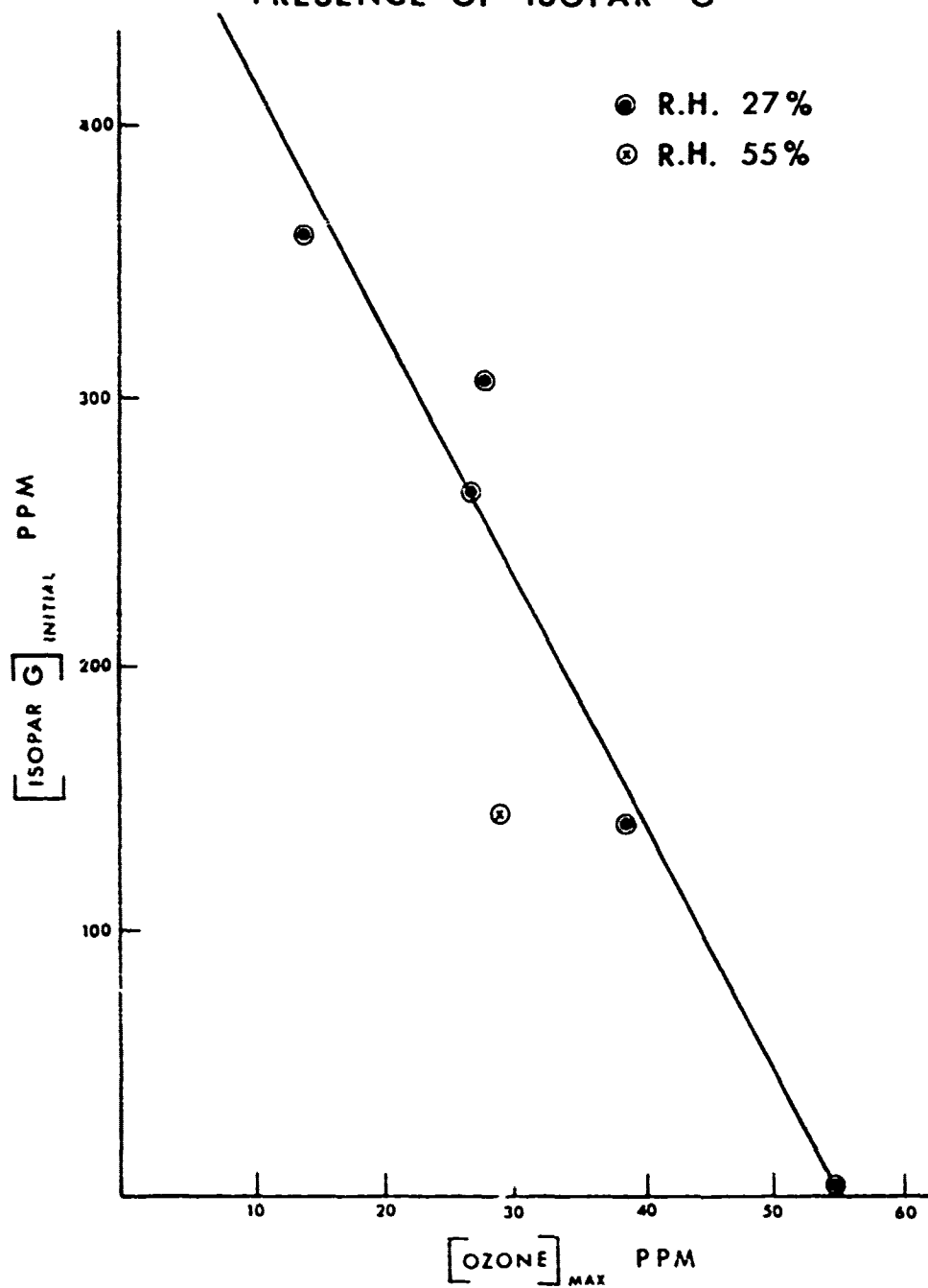


Table 7

Electrostatic Charging Characteristics of Mead 8313 Paper

<u>CDU #</u>	<u>Relative Humidity, %</u>	<u>Applied* Voltage</u>	<u>Measured † Voltage</u>	<u>Current mA</u>
1	33	-4500 ⁴	-2180	
1	33	-5500 ⁴	-2087	
1	33	-6800 ⁴	-1983	
1	33	+4500 ⁵	+2900	
1	33	+5500 ⁵	+3588	
1	33	+6800 ⁵	+3780	
1	33	-4500 ¹	-2230	
1	33	-4500 ^{1,3}	-2390	0.05
1	33	+4500 ²	+1644	
1	33	+4500 ^{2,3}	+2070	
1	51	+4500 ⁴	+105	0.09
1	51	+5500 ⁴	+87	0.10
1	51	+6800 ⁴	+74	0.12
1	51	+4500 ⁵	+195	0.05
1	51	+5500 ⁵	+195	0.10
1	51	+6800 ⁵	+280	0.12
1	68	+4500 ⁴	+313	0.10
1	68	+5500 ⁴	+318	0.10
1	68	+6800 ⁴	+205	0.15
5	31	-4500 ⁴	-1330	
5	31	-5500 ⁴	-2510	
5	31	-6800 ⁴	-5072	0.08
5	40	+4500 ⁵	+843	
5	40	+5500 ⁵	+2285	

5	40	+6800 ⁵	+3713	
5	37	-4500 ^{6,4}	-458	0.02
5	37	-5500 ^{6,4}	-516	
5	37	-6800 ^{6,4}	-1351	
5	35	+4500 ^{7,5}	+243	
5	35	+5500 ^{7,5}	+433	
5	35	+6800 ^{7,5}	+841	
5	72	-4500 ⁴	-173	
5	72	-6800 ⁴	-90	
5	74	+4500 ⁴	+113	0.02
5	74	-5500 ⁴	-23	0.03
5	74	-6800 ⁴	-110	0.04
5	72	-4500 ^{6,4}	-165	
5	72	-5500 ^{6,4}	-208	
5	72	-6800 ^{6,4}	-310	
5	72	+4500 ^{7,5}	+160	0.01
5	72	+5500 ^{7,5}	+220	0.02
5	72	+6800 ^{7,5}	+287	0.03
2	32	-4500 ⁴	-145	
2	32	-5500 ⁴	-173	
2	32	-6800 ⁴	-250	
2	32	+4500 ⁵	+223	
2	32	+5500 ⁵	+270	
2	32	+6800 ⁵	+333	0.04
2	32	-4500 ^{6,4}	-178	
2	32	-5500 ^{6,4}	-385	
2	32	-6800 ^{6,4}	-725	
2	32	+4500 ^{7,5}	+388	
2	32	+5500	+389	
2	32	+6800	+568	

Footnotes for Table 7

* Voltage applied to electrodes in the corona discharge unit

† Electrostatic potential measured on Mead 8313 paper

1. Positive lead floating; corona back plate grounded.
2. Negative lead floating; corona back plate grounded.
3. Oxygen enriched atmosphere.
4. ZnO coating facing negative electrode.
5. ZnO coating facing positive electrode.
6. Positive lead floating; plane electrode grounded.
7. Negative lead floating; plane electrode grounded.

Configuration

CDU #1 - wire to wire .

CDU #2 - wire to plane

CDU # 5 - point to plane .

coronas gave charging characteristics similar to the double corona.

If a comparison of the charging characteristics and the ozone production is made for the various corona units, the following points are observed. 1) Relative humidity reduces both the amount of ozone produced and the static potential buildup. 2) Isopar G reduces the amount of ozone produced, but does not affect the static potential buildup (12).

This suggests that the water is reacting with the negative charge carrying species, thus reducing its concentration and consequently the charge on the paper. If the charge carrier is also a precursor of ozone then the reduction of its concentration would also lead to a reduction of ozone produced, which is observed. In the case of Isopar-G the reduction of the ozone produced could be attributed directly to the interaction of ozone with Isopar G. This would account for the reduction of ozone and suggest that ozone is not the charge carrying species.

If the positive charge carrier is the proton, an increase in relative humidity would increase the hydration of this species thus decreasing its mobility.

B. 1. The Corona Discharge. In a series of articles (13,14) on a point to plane corona, G. W. Trichel described the character of the discharge. When the points were charged positively, it was shown that the current fluctuated in pulses which were of short duration. These bursts of current were random in time and intensity.

When the points were charged negatively, the points emitted current pulses which were constant in both magnitude and frequency. This observation resulted in a postulation that the character of the discharge was due to an interaction of the space charges of the individual points.

When these studies are applied to a wire to wire corona, the following macroscopic mechanism empirically can be stated. The following observations are stated for elucidation:

1. The field gradient, due to the diameter of the wires, is very high at the electrodes (15).
2. The process at the positive electrode collects electrons. Thus the current at this electrode is dependent upon the ionization potentials of the gases surrounding the wire.

3. The process at the negative electrode emits electrons; thus, the current at this electrode is dependent upon the work function of the metal.

The visual observation of the corona is presented in Figure 9. The visible emission at the positive electrode appears to be continuous and homogeneous for the length of the wire. An increase in the power supplied to this electrode results in an increase in emission.

At the negative electrode at reasonably high potentials, a series of beads form which are evenly spaced throughout the length of the wire. An increase in potential does not increase the number of beads, however, it does increase the intensity of visible emission. Further application of power results in the breakdown of the corona system into a spark.

B. 2. Toner Pickup. From a series of studies concerned with toner pickup with respect to the corona configuration and environment, a number of generalizations can be made. These are shown in Figures 10 and 11.

Figure 10B reflects the capability of this research group to charge the zinc oxide coated paper positively or negatively. The amount of charge and the charging area was greatly decreased in the case of a positive charging configuration.

Generally, the area which is charged by a corona is directly proportional to the time of charging (Figure 10A), the distance of the paper from the wire (Figure 11A), and the applied potential (Figure 11B).

The area of charging appears to exponentially decrease with an increase in relative humidity (Figure 11C).

Specific examples are shown in Figures 12 to 15. Figures 12 and 13 depict the differences between positive and negative charging. It should be noted that the charge homogeneity is much greater in the case of a positive charging configuration when compared to a negative charging configuration. The inhomogeneity in the case of the negative charge is due to the current being produced from the beads at this electrode. Further, in both cases as the distance of the paper from the electrode increases, the charging area increases. In comparing the prints in Figure 13 A, B, and C, the charged areas increased and the homogeneity of charge on the paper became more acceptable as the distance of the paper from the point was increased.

FIGURE 9 CORONA EMISSION CHARACTERISTICS

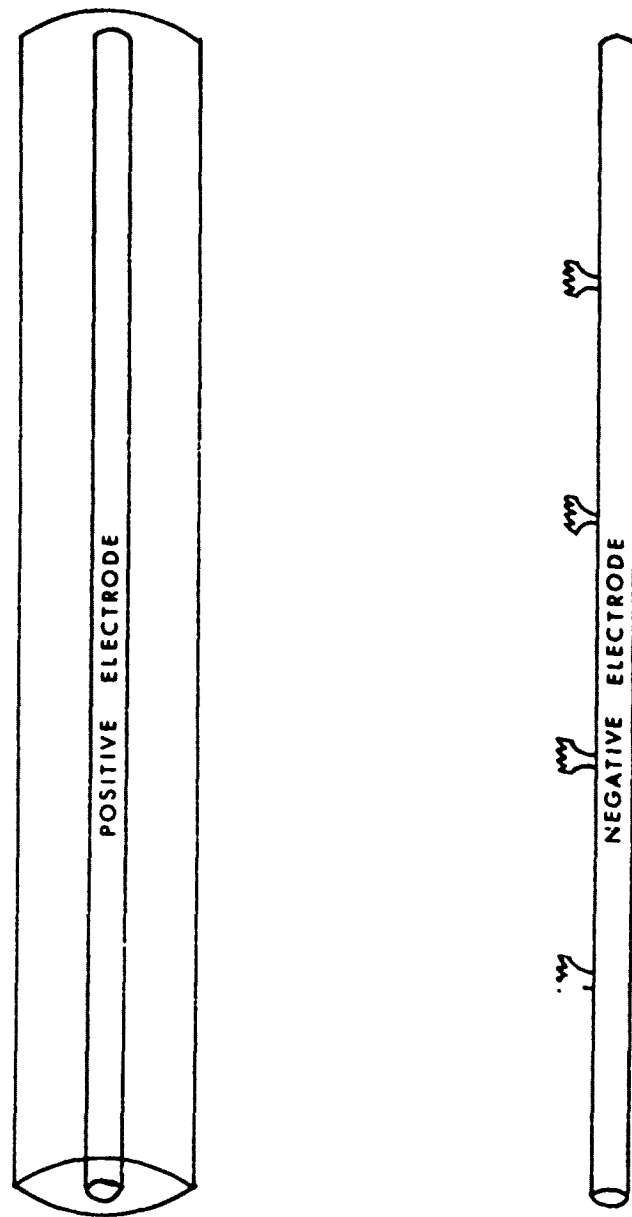


FIGURE 10 CHARGING CHARACTERISTICS I

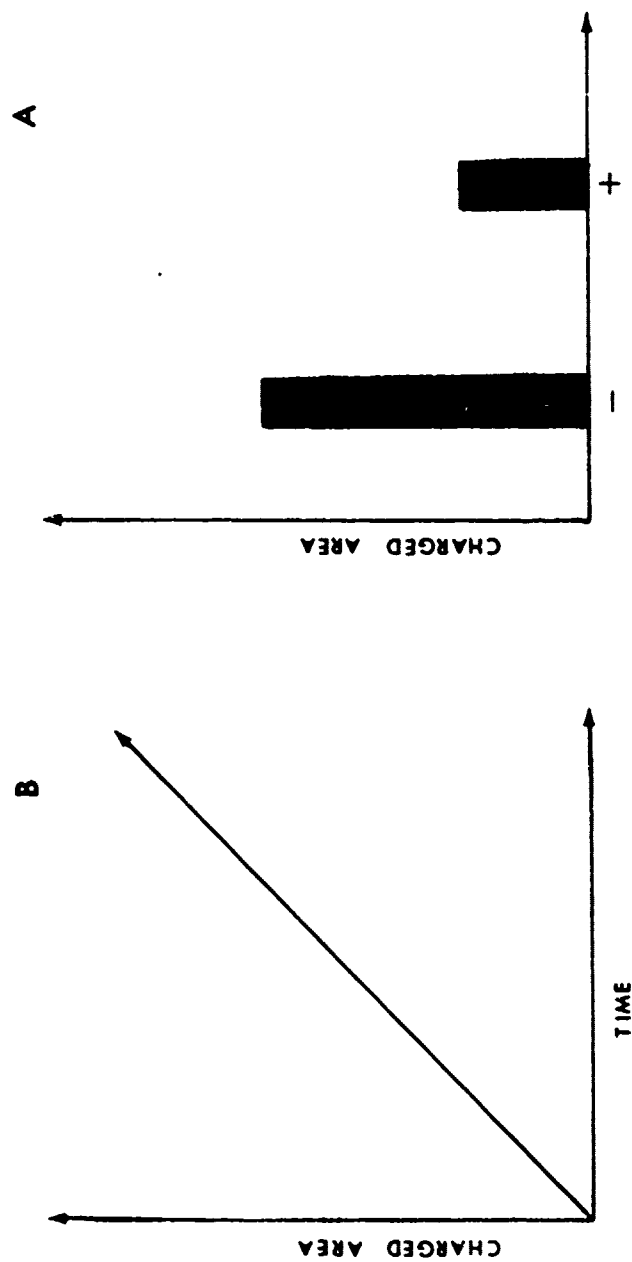
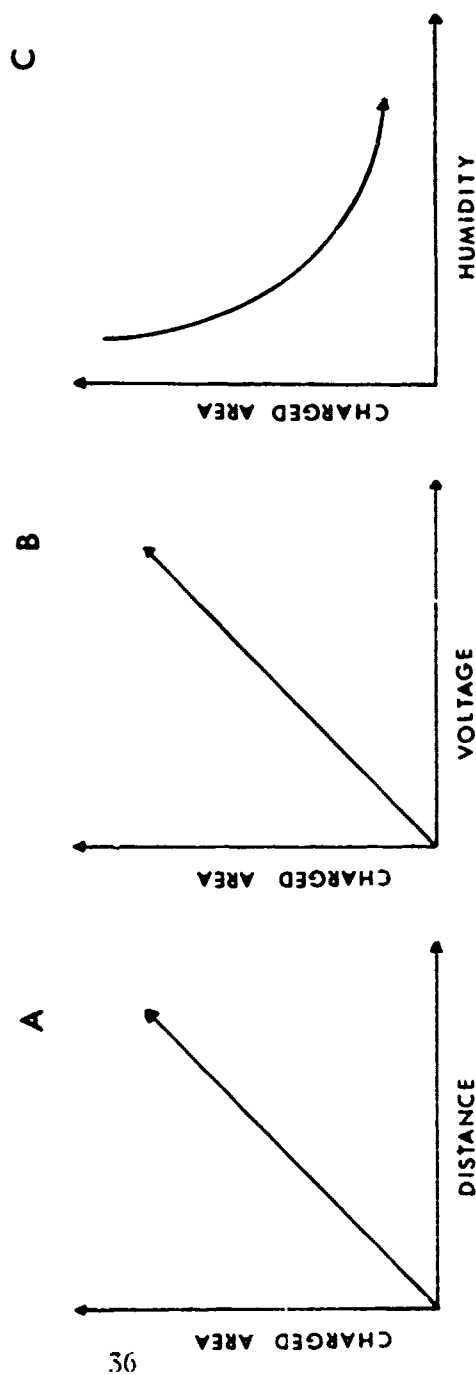


FIGURE 11 CHARGING CHARACTERISTICS II



Legend for Figure 12

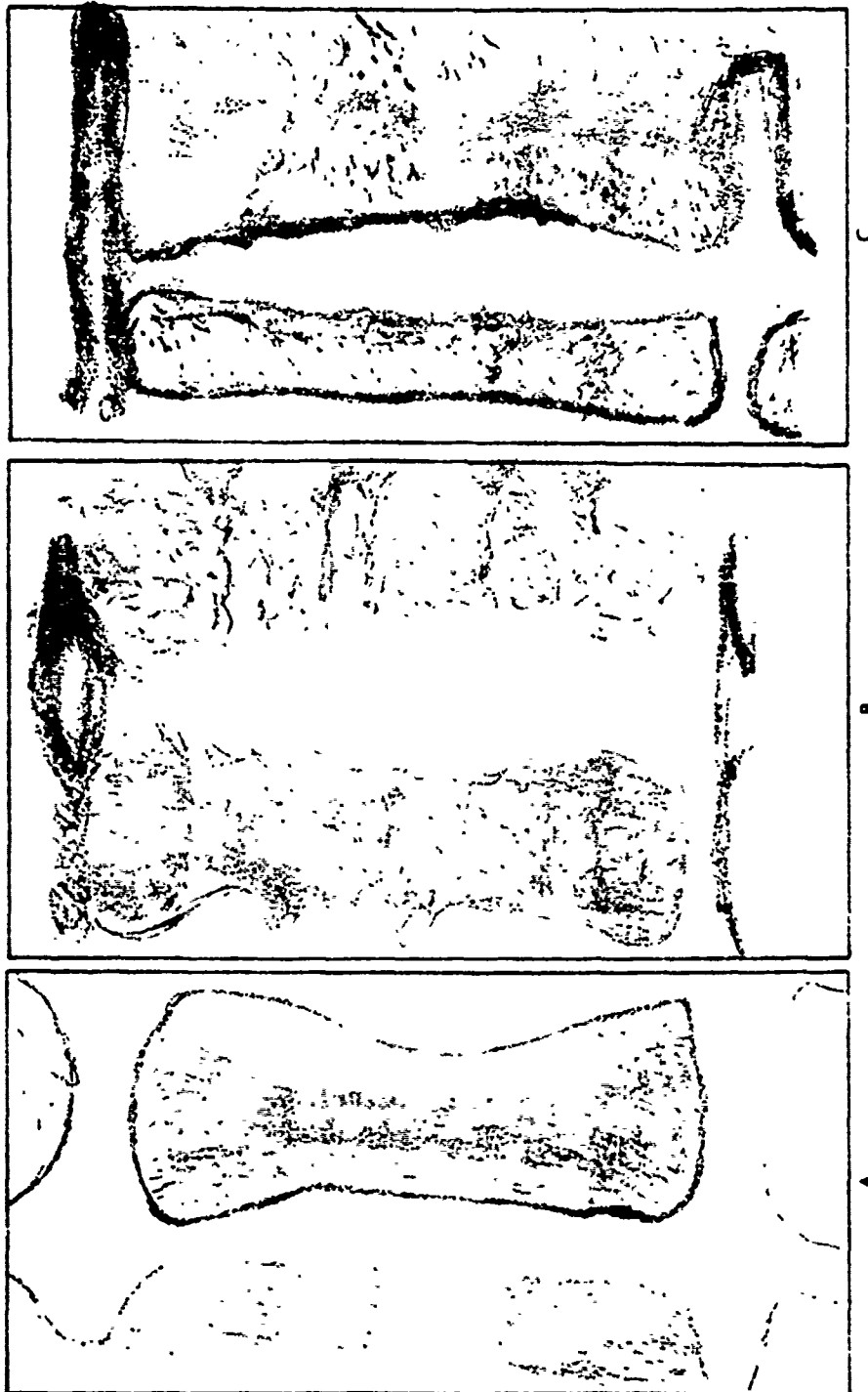
Current: 0.1 mamp.
Corona: wire to plane

Configuration: ZnO paper facing positive wire

- A. 0.5 cm from wire
- B. 1.0 cm from wire
- C. 1.5 cm from wire

The dark portions of the plate indicate the areas of particle pickup while the density reflects the amount. The white areas indicate no charge buildup.

FIGURE 12 TONER PICKUP I



Legend for Figure 13

Current: 0.1 mamp.

Corona: wire to plane

Configuration: ZnO paper facing negative wire

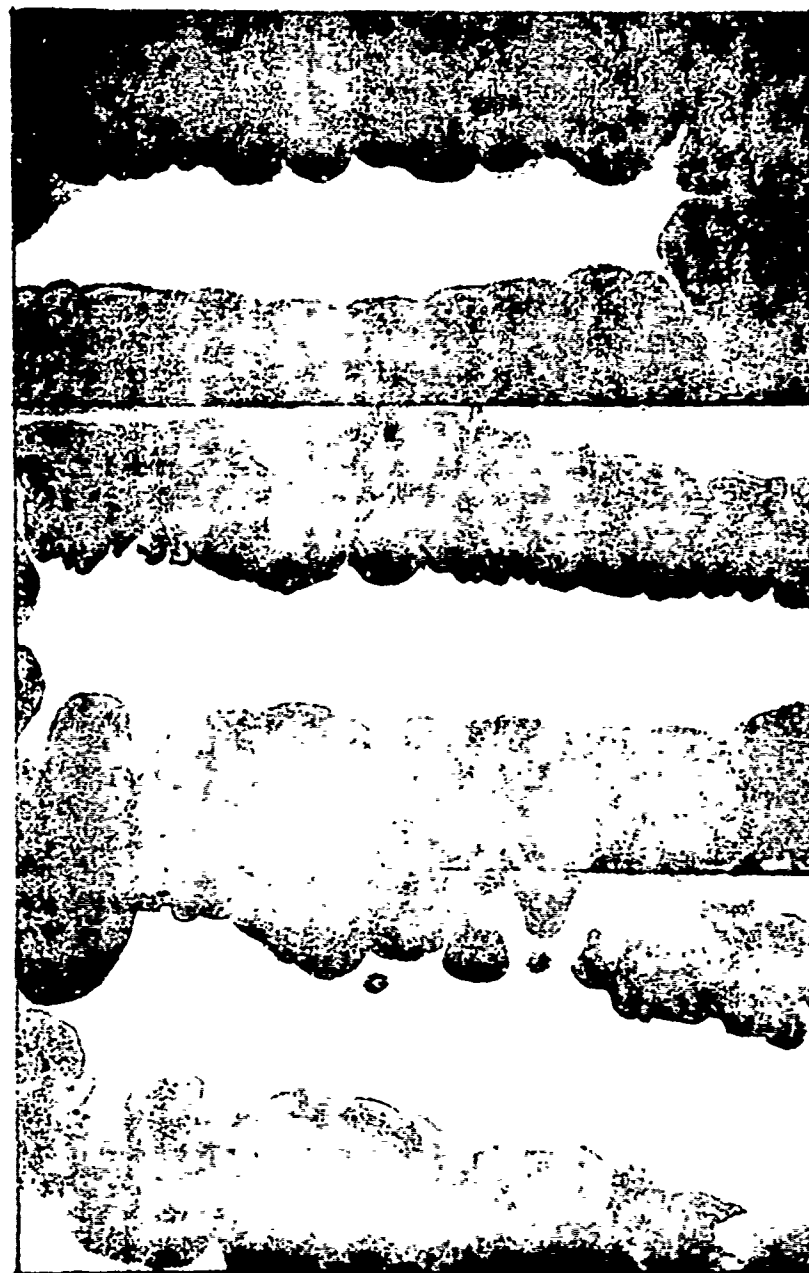
A. 0.5 cm from wire

B. 1.0 cm from wire

C. 1.5 cm from wire

The dark portions of the plate indicate the areas of particle pickup while the density reflects the amount. The white areas indicate no charge buildup.

FIGURE 13 TONER PICKUP II



In the case of a point to plane (Figures 14 and 15), it is apparent that:

1. The charged area on the paper is a function of distance from the electrode (Figure 15A and B)
2. The charged area on the paper is a function of the corona current (Figure 14A and 15B).
3. The charge homogeneity on the paper is poor.

The change in homogeneity can be explained by referring to the macroscopic mechanism of the corona. The point to plane corona that was used to charge the ZnO coated papers was designed to have a distance between the points of approximately 0.5 cm. Because of this it can be expected that the space charges of the individual points will interfere with one another. The greatest interference to the production of the current bead will be in the center of the point matrix, thus the least current will flow from this area. This effect is shown in Figures 14 and 15 where it appears that the maximum current flow is from the corners of the point matrix (minimum interference with adjoining space charges).

B. 3. Ion Currents. Attempts were made to both identify the charge carrier and the ion density within the corona. In the study on identification of the species in the corona, ultraviolet, visible, and infrared spectroscopy was used. The apparatus previously described was used for the ion current measurements (II.A.6).

From mass spectrometric measurements of other research groups, the charge carriers appear to be O_2^- and the hydrated proton $[H^+ (H_2O)_n]$. Our results, however,³ indicate that at least for the negative ion current, the charge carrier is directly related to the oxygen molecule. Although spectroscopic measurements in the ultraviolet and visible regions indicated the presence of excited nitrogen and the infrared region yielded no spectra (because of intensity), other studies indicate that the previous statement is justified. When the ZnO paper was charge in the presence of an enriched oxygen atmosphere the charge acceptance of the paper was increased. When all other gases (CO_2 , NO , N_2) were added to the environment surrounding the corona, a decrease in the charge acceptance of the paper was noted.

Ion currents were also measured for the point to plane corona in an attempt to observe the energetics and density of the ions. A typical plot of probe current as a function of applied voltage is

Legend for Figure 14

Current: 0.2 mamp.

Corona: point to plane

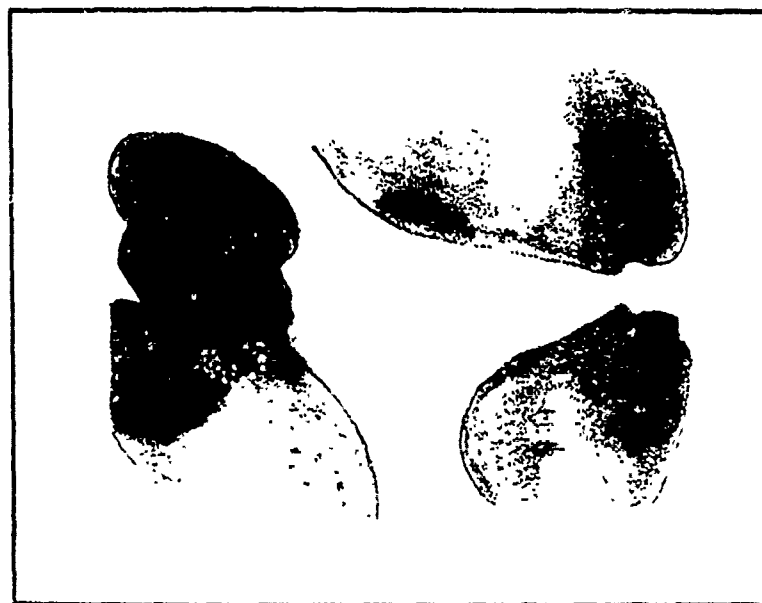
Configuration: ZnO paper facing negative points

A. 1.0 cm from points

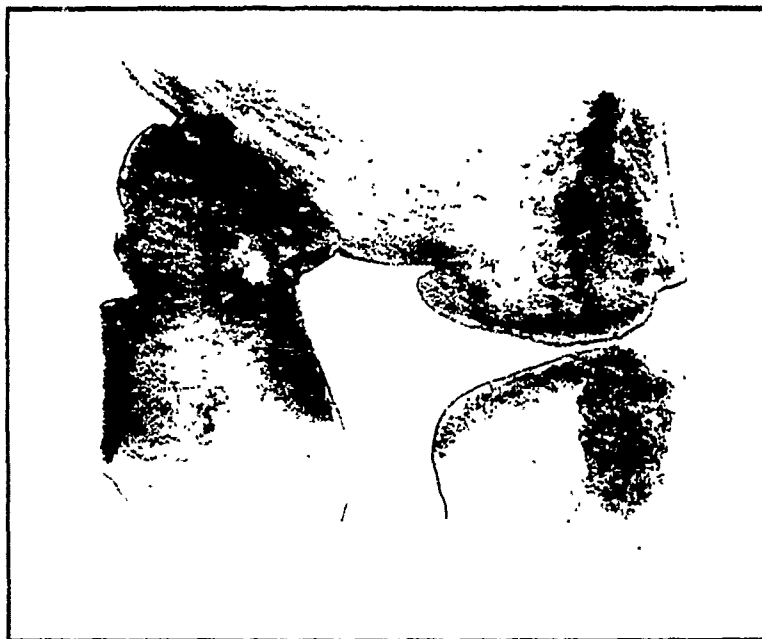
B. 1.5 cm from points

The dark portions at the plate indicate the areas of particle pickup while the density reflects the amount. The white areas indicate no charge buildup.

FIGURE 14 TONER PICKUP III



A



B

Legend for Figure 15

Current: 0.1 mamp.

Corona: Point to plane

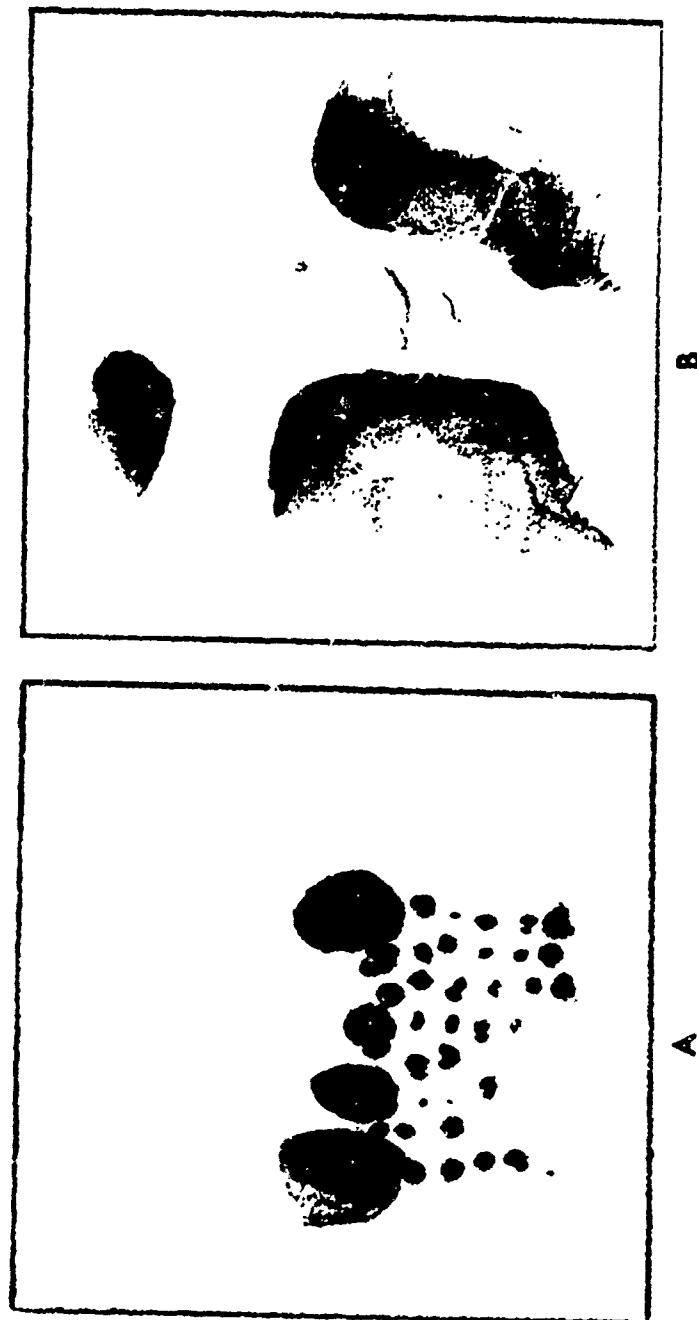
Configuration: ZnO paper facing negative points

A. 0.5 cm from points

B. 1.5 cm from points

The dark portions of the plate indicate the areas of particle pickup while the density reflects the amount. The white areas indicate no charge buildup.

FIGURE 15 TONER PICKUP IV



presented in Figure 16. Because of the current levels of the corona and the tendency for the probes to act as a ground (resulting in a spark), measurement of the characteristics were quite difficult. From these studies, however, a number of qualitative conclusions can be made.:

1. The average energy of the ions decreases as the distance from the electrodes increases.
2. The average ion current per unit volume decreases as distance from the electrodes increases (Figure 17).
3. The corona current fluctuates directly with the signal applied to the corona itself (Figure 18).

All of these observations are consistent with other observations.

IV. CONCLUSIONS

A number of conclusions can be obtained from this project: The remaining discussion is applied to (A) the type of charging unit which will produce the most homogeneous charge, (B) environmental effects, and (C) major recommendations.

A.1. Wire Charging Configuration. As was previously described, a wire configuration as opposed to a point configuration is preferred, especially for negative charging. Because of the interaction of the point emitters an uneven current flow exists resulting in inhomogeneous charging characteristics. It is the impression of these researchers that the wire to plane CDU would be preferred also in the positive charging mode. The point to plane CDU are difficult to fabricate and the wire CDU results in very inhomogeneous charging of the plate.

A.2. There is a good indication that both the positive and negative electrodes (point, wire) produce ozone in fairly high concentrations. The amount of this material produced can be decreased by replacing the point or wire counter electrodes with a plane. It appears that the ozone is produced in the corona because the high potential gradients in the system. In the case of the wire to wire, the point to point, or wire to point the gradient is duplicated at both electrodes. By replacing one electrode with a plane the potential gradient can be reduced sufficiently to minimize or totally eliminate ozone production at the electrode.

A.3. A Positive Charging Configuration. From the toner pickup studies it becomes obvious that a positive charging configuration is preferred to the presently accepted negative charging. Since the

FIGURE 16 CURRENT-VOLTAGE CHARACTERISTIC OF CORONA

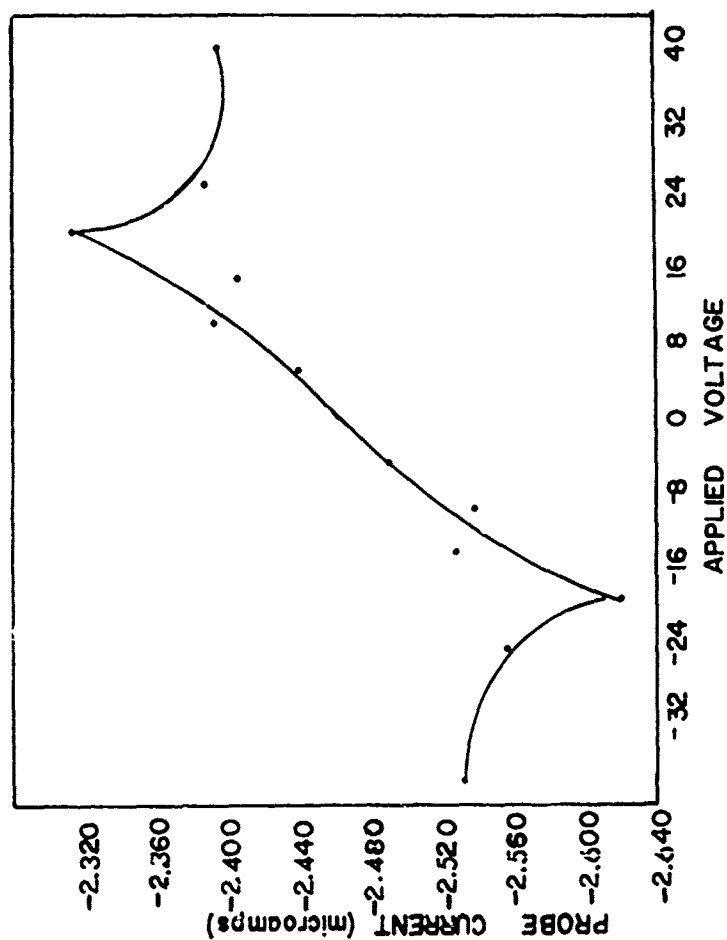
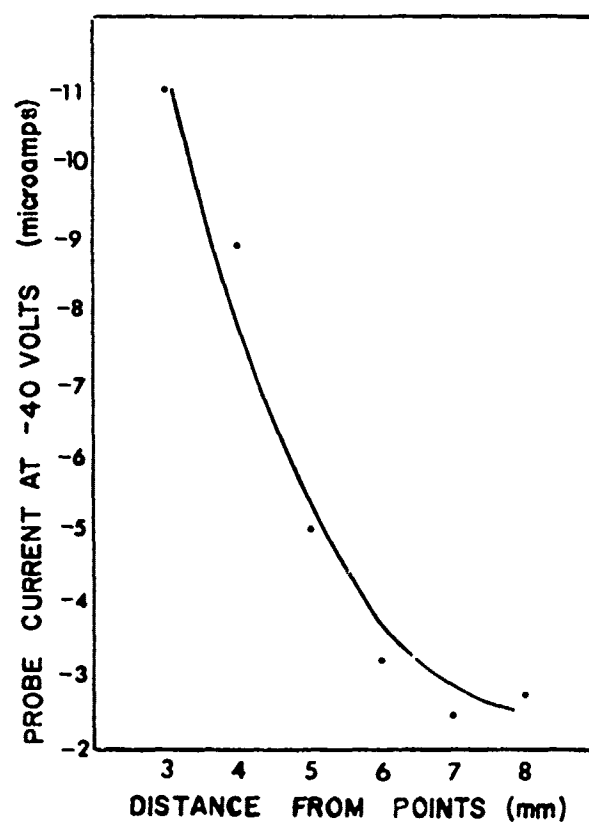
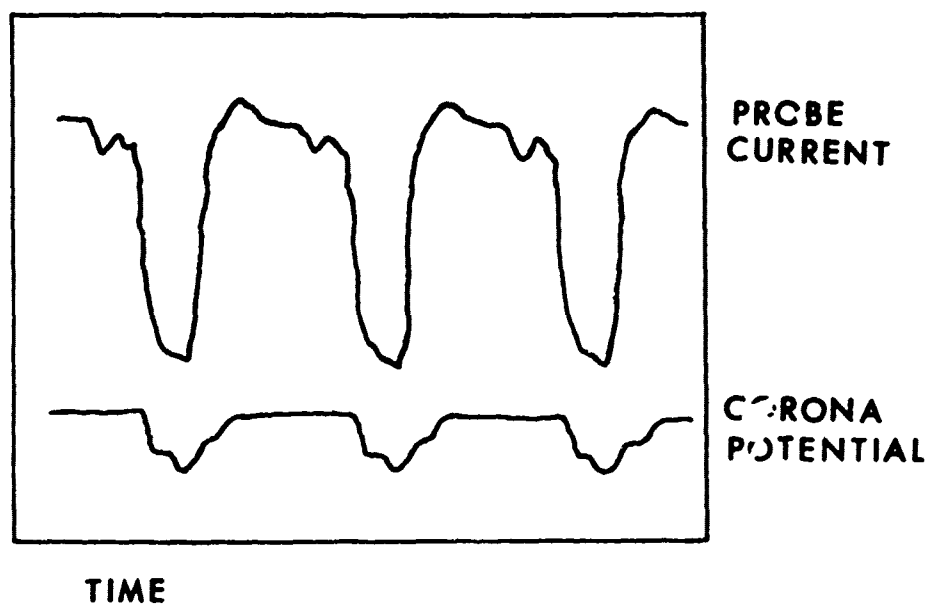


FIGURE 17 CURRENT-DENSITY
PROFILE OF CORONA



**FIGURE 18 TIME DEPENDENCE OF
CORONA DISCHARGE**



majority of the current that emanates from the negative electrode comes from the luminous "beads", inhomogeneity in charging of the paper is observed.

A positive wire, on the other hand, produces a sheath of current carriers along the wire, resulting in a more homogeneous charging of the substrate exposed to the corona.

A.4. Distance of Paper from Corona. The term charging efficiency should be used at this point in the discussion, and it will be operationally defined as the ratio of useful charge carriers reaching the plate to the total number of charge carriers produced. As the corona charging unit is moved to a position farther from the plate, the efficiency decreases. At the same time in order to maintain the same rate of charging, the power supplied to the wire must be increased. Thus, the overall effect is one of production of increased concentrations of ozone as the distance between the charging wire and plate is increased.

A practical example of this may be taken from a comparison of the current required for the Army RACOMS Printer and the Xerox machine. The charging units in the Xerox machine are in very close proximity to the selenium drum whereas the Army printer's separation is much larger. The current levels required in the Xerox machine are a factor of 10^2 to 10^3 less than required by the Army printer. Thus, the ozone production in the Xerox process is minimized.

B. Environmental Effects. This section is applied to those parameters which affect the production of ozone.

B.1. Production of Ozone. The following conclusions are made with respect to the production of ozone:

1. The equilibrium concentration of ozone increases with an increase in power supplied to the corona discharge unit. As the distance between the electrodes of the corona increases more power must be supplied to the unit to maintain an equivalent ion density at the paper interface. Thus, as the distance between the electrodes increases, the ozone production increases.
2. The equilibrium concentration of ozone is dependent upon the type of metal used for the electrodes. Certain metals, such as platinum, appear to produce ozone at a higher rate than others, such as copper (see Figure 7).

3. The ozone production is dependent upon corona configuration. Distance (for equivalent ion currents per unit volume) is a very important consideration as discussed previously. The type of counter electrode used governs, to some extent, the amount of ozone produced. In the case where the counter electrode is a plane, the production of ozone is decreased appreciably. This also indicates that both electrodes produce ozone in this system.
4. An increase in humidity decreases the ozone production (see section III.A.2.)
5. An increase in hydrocarbon content of the atmosphere decreases the equilibrium concentration of ozone (see section II.A.4.). Presumably this is due to an oxidation reaction which occurs in the vapor state between the two compounds. Although addition of a gaseous reactive material appears to be a method of reducing the ozone concentration, care must be taken in applying this to the printer. Studies of the effects of these reactions products (12) indicate that the reproduction process can be seriously hindered by the presence of polar compounds.

C. MAJOR RECOMMENDATIONS

C. 1. Charging Configuration. Develop a process in which a positive wire charging configuration can be used (such as the IFAX process, Horizons Research).

C.2. Ozone Production. Develop a process which reduces the production of ozone in the unit. This can be accomplished by:

C.2. a. Decreasing the distance between the charging wire and the plate.

C.2.b. Reducing ozone concentration after formation by venting or using an efficient "getter" for the ozone.

LITERATURE CITED

1. Basic Manual of Applications and Laboratory Ozonation Techniques; 1st Rev., The Welsbach Corp., Ozone Processes Div., Philadelphia, PA. 1958.
2. D. A. Skoog and D. M. West, Fundamentals of Analytical Chemistry, Holt, Rinehart and Winston, New York, N.Y., 1966.
3. J. W. Berry, Spectrographic Determinations of Anions, Thesis, University of Iowa, Iowa City, Iowa 52240
4. J. Hartmann, *Astrophys. J.* 8, 218 (1898).
5. R. A. Sawyer, Experimental Spectroscopy, Dover Publications, Inc. New York, 1963.
6. I. Langmuir, H. Mott-Smith, Jr., *General Electric Review*, XXVII, 449 (1924).
7. I. Langmuir, H. Mott-Smith, Jr., *General Electric Review*, XXVII, 762 (1924).
8. I. Langmuir, H. Mott-Smith, Jr., *General Electric Review*, XXVII, 616 (1924).
9. I. Langmuir, H. Mott-Smith, Jr., *General Electric Review*, XXVII, 811 (1924).
10. C. F. Gallo, J. E. Germanos, J. E. Courtney, *Applied Optics Supplement: Electrophotography* 3, 111 (1969).
11. Chemical Kinetics of Gas Reactions, Pergamon Press, New York (1964).
12. C. W. Frank, J. K. Stille, F. E. Green, G. B. Dreher, "A Corona Study Relevant to Electrostatic Printing Process" USAETL Final Report ETL-CR-71-22 under contract Number. DAAK02-71-C-0027, November, 1971.
13. G. W. Trichel, *Phys. Rev.* 54, 1078 (1938).
14. G. W. Trichel, *Phys. Rev.* 55, 382 (1939).
15. Reactions Under Plasma Conditions, M. Venugopalan, Ed., Wiley-Interscience, New York 1971.